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(19)

(54) STYRENE BUTADIENE RUBBER COMPOSITIONS

(71) We, THE INTERNATIONAL SYNTHETIC RUBBER COMPANY LIMITED, a British Company of Brunswick House, Brunswick Place, Southampton, Hampshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions made by blending solid polymers. Styrene butadiene co-polymers (S.B.R.) produced by polymerisation in a hydrocarbon medium with an organometallic anionic catalyst have somewhat lower tensile properties that the equivalent co-polymers produced by emulsion processes. In many applications this is not of great importance and the superior processing properties of solution SBR dictate choice. However, in certain applications, for example conveyor belting, emulsion polymer is generally used to achieve the best possible tensile properties.

Emulsion copolymers and solution copolymers differ mainly in respect of their microstructure and MW distribution. There is in fact no convincing evidence to connect the observed differences with microstructure and it is generally held that the differences are due rather to the substantial difference in molecular weight distribution between the two types of copolymer.

Solution SBR prepared with a lithium alkyl catalyst is characterised by a relatively narrow distribution whereas the emulsion polymer presents a broad distribution curve extending beyond 10^6 molecular weight. Emulsion polymer also contains a proportion of material having an apparent molecular weight of several millions. This can be recovered from hydrocarbon solution by microfiltration amd may arise in part through slight cross linking of large polymer chains.

Tensile properties of SBR increase with increasing Mooney value and it is possible to match an emulsion SBR with a solution SBR, of for example, 20—30 Mooney points higher. This, however, is not acceptable to the compounder because of the greatly increased processing difficulties. The problem is to match physical properties at the same Mooney level, which is the level acceptable to the compounder. Normally this level is in the range 20—100 Mooney M_L 1 + 4 at 100°C.

One approach to the problem is to carry out a "coupling" reaction. Such reactions are well known. For example, an active (live) polymer-Li species (obtained using a lithium alkyl catalyst) is reacted with a substance having two or more functional groups, e.g.

$$CH_2Cl_2, SiCl_4, SnCl_4.$$

The effect is to broaden molecular weight distribution and, in the case of coupling where three or more chains are found, to produce a high molecular weight fraction of branched structure which does not increase solution or Mooney viscosity to the extent that would be the case with linear polymer of the same high molecular weight. Where a metallic halide is employed it is claimed that a high Mooney polymer can be made which breaks down rapidly on milling, combining the advantages of higher tensile properties with easy processing.

A disadvantage of this approach is that polymer chains must be "live" when coupling is effected, so monomer conversion cannot be taken to completion. Another disadvantage is that the polymer thus produced is, we believe, still not fully comparable to the equivalent emulsion SBR.

Simply broadening molecular weight distribution at a given Mooney level does not improve tensile properties and indeed may result in a reduction. This is also true if blends of polymers having Mooney levels about the desired mean are used, when the higher Mooney polymer has an ML 1 + 4 less than about 100. We have found, however, that if a solution SBR of higher than normal Mooney viscosity, having a significant proportion of polymer with

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Molecular weight about 500,000 and preferably above 10^6, is modified by blending with a solution polymer of low Mooney viscosity, an enhancement of tensile properties may be achieved.

According to the present invention we provide a polymer composition having a Mooney viscosity (ML_{1+4} 100°C) of 20 to 100 comprising (A) a styrene butadiene rubber having a Mooney viscosity on the same basis of at least 100 modified with (B) a styrene butadiene rubber having a Mooney viscosity of 1 to 32 on the same basis, in which the proportion of polymer (A) is at least 10% by weight of the composition, each rubber being prepared by solution polymerisation using a lithium alkyl catalyst, the tensile strength of the polymer composition, after vulcanisation, being greater than that of a styrene butadiene rubber prepared by solution polymerisation using a lithium alkyl catalyst of the same compound Mooney as that of the polymer composition, vulcanised under the same conditions.

Preferably, the Mooney Viscosity of the composition is 40—80 and preferably the said first component polymer comprises at least 50% by weight of the composition.

The second component polymer has a Mooney viscosity in the range 1 to 32 Mooney. The second component polymer is solid and therefore the limit of 1 is dictated by this factor. Preferably the difference between the viscosities of polymers (A) and (B) is as large as possible. It is especially preferred that the second component polymer has a Mooney Viscosity of 1 to 15 Mooney.

A simple binary distribution is sufficient to achieve the result desired. However, ternary and even more complex blends could be used. Generally best properties are achieved where blends of as widely differing Mooney as practicable are employed and a binary mixture is clearly to be preferred.

Blends can be made by mixing solutions of polymers or, of course, from the isolated polymers. It is possible however to make the desired product in a continuous reactor, provided no great degree of back mixing occurs, by sequential addition of catalyst to the polymerising mixture. Thus if the incoming feed is initiated with catalyst to give polymer of >100 Mooney at ~70% conversion, then extra catalyst is added to produce largely low Mooney polymer (say 7—10 M) the final polymer solution will contain an intimate mixture of the high and low Molecular Weight polymers.

The polymer molecular weights can be readily identified using gel permeation chromatography techniques.

EXAMPLES.

Examples 1—7.

Samples of lithium alkyl polymerised solution SBR polymers of 25% by weight styrene were made by batch polymerisation. The characteristic molecular weight distribution curve of each was measured using gel permeation chromatography and is illustrated in the accompanying drawings, wherein:

Figs. 1 to 3 are respectively the molecular distribution curves for the low molecular weight SBR's used as component (B) and having Mooneys (ML_{1+4} at 100°C) of 7, 15 and 32, and

Figs. 4 and 5 are respectively the molecular distribution curves for the high molecular weight SBR's used as component (A) and having Mooneys (ML_{1+4} at 100°C) of 120 and 149.

Blends were prepared by mechanical blending of two polymers of different base Mooneys, as shown in Table I, to give, as near as practicably possible, a resultant Mooney for the composition of 50.

The blends were compounded to the following formulation:

	Solution Polymer	Emulsion Polymer (comparison)
Polymer	100 parts by wt.	100 parts by wt.
Carbon Black N 110	45 ,,	40 ,,
Highly Aromatic Process Oil	5 ,,	5 ,,
Zinc Oxide	3 ,,	3 ,,
Stearic Acid	2 ,,	2 ,,
Sulphur	1.5 ,,	2 ,,
N-tertiary butyl-benzothiazole 2-sulphenamide	0.9 ,,	0.9 ,,

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Samples of each composition were press cured in a microtensile mould at 145°C to optimum cure time. The tensile strength (T/S) of each vulcanisate was measured and is given in Table 1.

The results where 7 Mooney material was used to adjust final Mooney are particularly striking. (Examples 1 and 2). 7 Mooney polymer on its own has very poor tensile properties but when blended with 120 Mooney polymer, the tensile properties are almost as good as can be achieved with the 120 Mooney polymer used alone. The blend, having a Mooney of 50, is however much easier to process.

TABLE I

Tensile Strength of Bimodal Distribution Blends

Example No.	Mooney ML_{1+4} 100°C		Weight Ratio	Mooney of Blend ML_{1+4} 100°C	T/S (p.s.i.g.)
	Low MWt. SBR	High MWt. SBR			
1	7	120	35/65	50	4600
2	7	149	50/50	48	4300
3	15	149	58/42	50	4300
4	15	149	55/45	53	4600
5	32	120	80/20	48	4300
6	32	149	80/20	50	4400
7	15	120	50/50	48	4200

For comparison the Tensile Strength of normal SBR's is:—

	T/S (p.s.i.g.)	Mooney ML
Emulsion SBR ~	4400 — 4600	55
Solution SBR ~	4000 — 4200	55

EXAMPLES 8 to 25.

(Examples 8, 9, 10, 15 to 17 and 21 to 23 are for comparison since the Mooney viscosity of the high molecular weight polymer is below 100)

Sample SBR polymers containing 25% bound styrene were prepared in solution using lithium butyl as initiator and a potassium-Michler's ketone complex as randomising agent. The Mooney viscosity of each was measured and is given in Table II.

TABLE II

Low Mooney Polymer		High Mooney Polymer	
	Raw Polymer		Raw Polymer
Sample	ML_{1+4} at 100°C	Sample	ML_{1+4} at 100°C
A	7	H	75
B	9	J	80
D	15	L	120
E	32	M	145
		N	149

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Polymer compositions were prepared by blending samples of a low Mooney polymer and a high Mooney polymer as shown in Table III and compounding to the formulation given in Examples 1 to 7. After vulcanisation for 35 minutes at 145°C the modulus at 300% (M 300), tensile strength (T/S) and elongation at break (EB) were measured for each composition and the results are given in Table III.

TABLE III

Example No.	Blend No.	Low MWt. Polymer	High MWt. Polymer	Blend ML4	M300	T/S	EB
8	1	30% A	70% H	41	1010	3600	640
9	2	20% A	80% H	51	810	3730	750
10	3	25% A	75% J	50	690	3560	790
11	4	35% A	65% L	50	860	4060	720
12	5	50% A	50% N	48	1300	4300	640
13	6	50% B	50% M	59	1180	4590	660
14	7	50% B	50% N	59	1230	4150	620
15	8	40% D	60% H	43	860	3820	730
16	9	30% D	70% H	51	830	3600	740
17	10	35% D	65% J	48	690	3470	820
18	11	50% D	50% L	48	850	3860	720
19	12	58% D	42% N	50	1290	4250	620
20	13	55% D	45% N	53	1390	4560	610
21	14	70% E	30% H	46	810	3650	740
22	15	60% E	40% H	51	840	4200	760
23	16	65% E	35% J	48	750	3720	770
24	17	80% E	20% L	48	910	4110	690
25	18	80% E	20% N	50	1080	4060	670

Bimodal polymers made by blending linear solution SBR of greater than 120 Mooney with linear solution SBR of less than 25 Mooney, in which the proportion of high molecular weight component lies between 20—80% show a tensile strength higher than expected. Tensile strengths significantly higher than those of the corresponding narrow MWD polymers are exhibited by blends containing approximately equal proportions of 8 to 12 Mooney and substantially 150 Mooney polymer. The viscosity of such blends is in the approximate range 50—60 ML_4, and the compound viscosity of the blends is normal.

WHAT WE CLAIM IS:—

1. A polymer composition having a Mooney viscosity (ML_{1+4} 100°C) of 20 to 100 comprising (A) a styrene butadiene rubber having a Mooney viscosity on the same basis of at least 100 modified with (B) a styrene butadiene rubber having a Mooney viscosity of 1 to 32 on the same basis, in which the proportion of polymer (A) is at least 10% by weight of the composition, each rubber being prepared by solution polymerisation using a lithium alkyl catalyst, the tensile strength of the polymer composition, after vulcanisation, being greater than that of a styrene butadiene rubber prepared by solution polymerisation using a lithium alkyl catalyst of the same compound Mooney as that of the polymer composition, vulcanised under the same conditions.

2. A composition according to claim 1 having a Mooney viscosity of 50 to 60 Mooney.

3 A composition according to claim 1 or claim 2 in which the Mooney viscosity of polymer (B) is 1 to 15.

4. A composition according to claim 3 in which the Mooney viscosity of polymer (B) is 8 to 12.

5. A composition according to any

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preceding claim in which the Mooney viscosity of polymer (A) is 100 to 150.

6. A composition according to any preceding claim in which the proportion of polymer (A) is at least 50% by weight of the composition.

7. A composition according to any one of claims 1 to 5 in which the proportion of polymer (A) is 20 to 80% by weight of the composition.

8. A composition according to any preceding claim prepared by mechanically blending the polymers.

9. A composition according to any preceding claim prepared by sequential addition of lithium alkyl to the live polymerisation of polymer (A) to prepare polymer (B) *in situ*.

10. A composition according to claim 1 substantially as hereinbefore described with reference to any one of Examples 1 to 7, 11 to 14, 18 to 20, 24 and 25.

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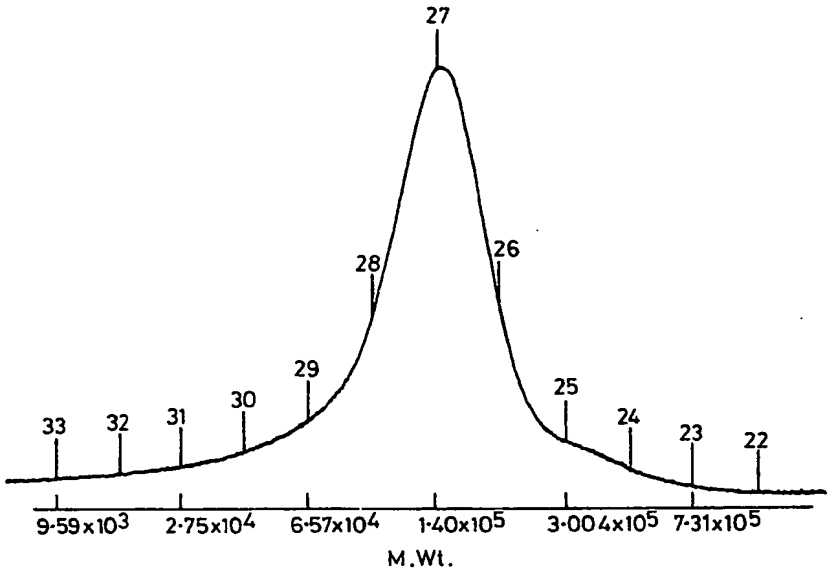
1501378 COMPLETE SPECIFICATION

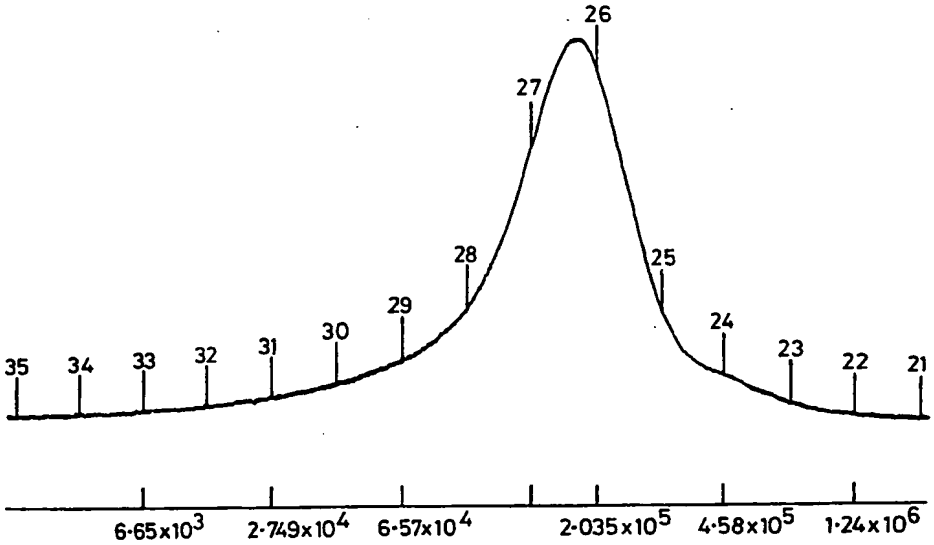
3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1



ML 1+4 = 7

FIG. 1



ML 1+4 = 15

FIG. 2

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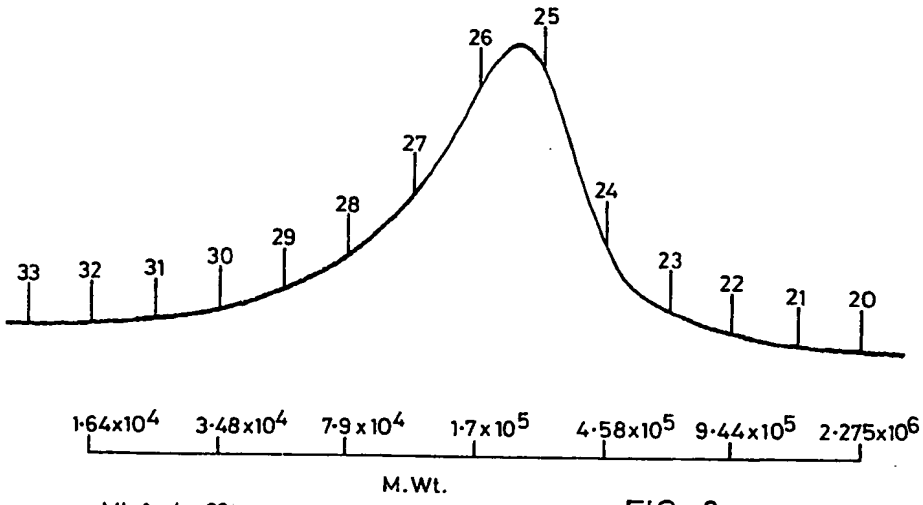
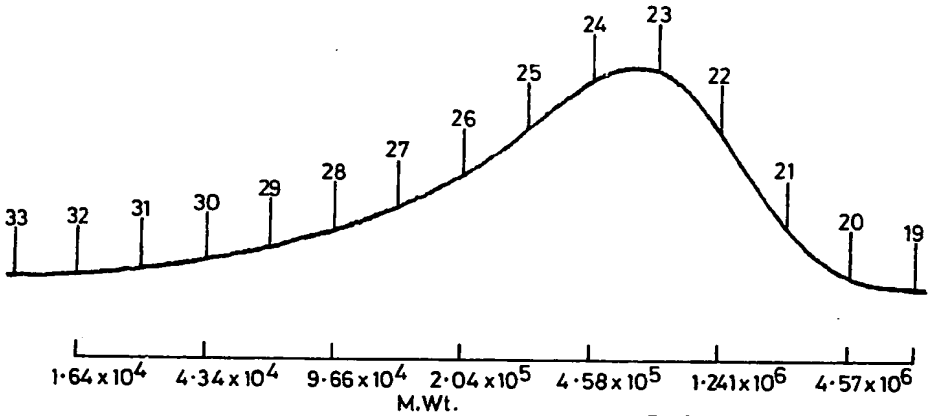


ML 1+4=32

FIG. 3



ML 1+4=120

FIG. 4

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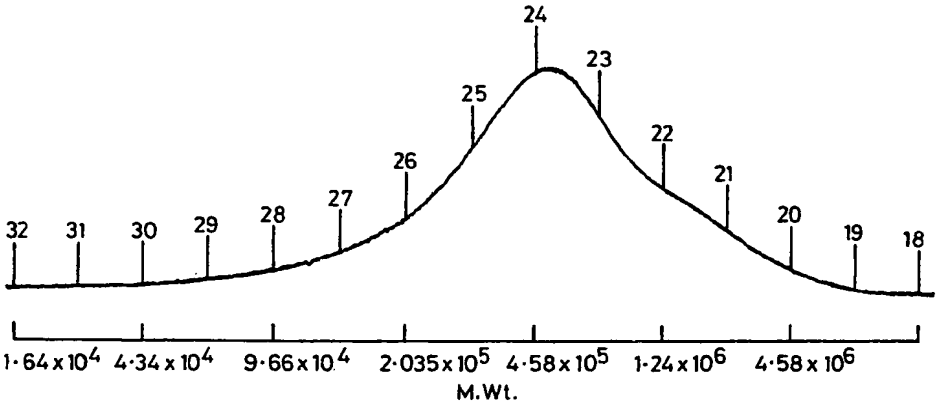

ML 1+4=149

FIG. 5

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